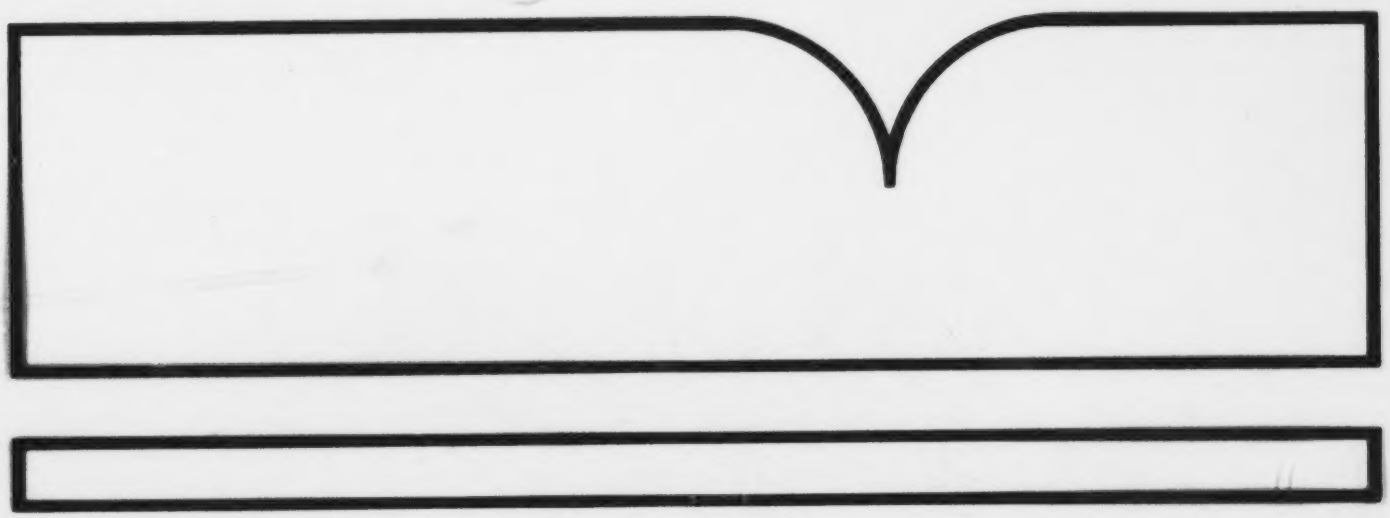
PB80-209778

Reference Method 24-Determination of Volatile Matter Content, Water Content, Density, Volume Solids, and Weight Solids of Surface Coatings Reference Method 25-Determination of Total Gase

(U.S.) Environmental Protection Agency
Research Triangle Park, NC

Jul 80



U.S. Department of Commerce
National Technical Information Service
NTIS

PB80-208228

United States
Environmental Protection
Agency

Office of Air Quality
Planning and Standards
Research Triangle Park NC 27711

EPA-450/3-79-030c
July 1980

Air

EPA

Reference Methods 24 and 25 — Background Information for Promulgated Test Methods

REPRODUCED BY
NATIONAL TECHNICAL
INFORMATION SERVICE
U.S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA. 22161

NSPS

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO.	2.	3. RECIPIENT'S ACCESSION NO.
EPA/450-3-79-030c		

4. TITLE AND SUBTITLE	5. REPORT DATE
Reference Methods 24 and 25 - Background Information for Promulgated Test Methods	June 1980
	6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S)	8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS Office of Air Quality Planning and Standards US Environmental Protection Agency Research Triangle Park, NC 27711	10. PROGRAM ELEMENT NO.
	11. CONTRACT/GRANT NO.
12. SPONSORING AGENCY NAME AND ADDRESS DAA for Air Quality Planning and Standards Office of Air, Noise, and Radiation US Environmental Protection Agency Research Triangle Park, NC 27711	13. TYPE OF REPORT AND PERIOD COVERED Final
	14. SPONSORING AGENCY CODE EPA 200/04

15. SUPPLEMENTARY NOTES

16. ABSTRACT

Reference Method 24 is used to determine the volatile organic compound (VOC) content of coating materials, and Reference Method 25 is used to determine the percentage reduction of VOC emissions achieved by emission control devices. These methods were proposed on October 5, 1979, as an appendix to the proposed standards of performance for automobile and light-duty truck surface coating operations. This document contains information on the public comments made after proposal and EPA responses to the comments.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Air pollution Pollution control Surface coating operations Test methods Volatile organic compounds (VOC)	Air Pollution Control	13 B

18. DISTRIBUTION STATEMENT	19. SECURITY CLASS *(This Report)*	21. NO. OF PAGES
Unlimited	Unclassified	20
	20. SECURITY CLASS *(This page)*	22. PRICE
	Unclassified	

EPA Form 2220-1 (Rev. 4-77) PREVIOUS EDITION IS OBSOLETE

EPA-450/3-79-030c

Reference Method 24 — Determination of Volatile Matter Content, Water Content, Density, Volume Solids, and Weight Solids of Surface Coatings

Reference Method 25 — Determination of Total Gaseous Nonmethane Organic Emissions as Carbon

Background Information for Promulgated Test Methods

Emission Standards and Engineering Division

U.S. ENVIRONMENTAL PROTECTION AGENCY
Office of Air, Noise, and Radiation
Office of Air Quality Planning and Standards
Research Triangle Park, North Carolina 27711

July 1980

This report has been reviewed by the Emission Standards and Engineering Division, Office of Air Quality Planning and Standards, Office of Air, Noise, and Radiation, Environmental Protection Agency, and approved for publication. Mention of company or product names does not constitute endorsement by EPA. Copies are available free of charge to Federal employees, current contractors and grantees, and non-profit organizations - as supplies permit - from the Library Services Office, MD-35, Environmental Protection Agency, Research Triangle Park, NC 27711; or may be obtained, for a fee, from the National Technical Information Service, 5285 Port Royal Road, Springfield, VA 22161.

Publication No. EPA-450/3-79-030c

TABLE OF CONTENTS

		Page
Chapter 1.	SUMMARY	1-1
	1.1 SUMMARY OF CHANGES SINCE PROPOSAL	1-2
Chapter 2.	SUMMARY OF PUBLIC COMMENTS	2-1
	2.1 TEST METHODS	2-1
	TABLE 2-1. LIST OF COMMENTERS ON PROPOSED TEST METHODS	2-7

CHAPTER 1

SUMMARY

On October 5, 1979, as an appendix to the proposed standards of performance for automobile and light-duty truck surface coating operations, the U. S. Environmental Protection Agency published in the FEDERAL REGISTER (44 FR 57792) reference methods for analyzing the solvent content of coatings [Reference Method 24 (Candidate 1) and (Candidate 2)] and for determining the percentage reduction of volatile organic compound (VOC) emissions achieved by emission control devices (Reference Method 25). These test methods were proposed under the authority of Sections 111 and 114 of the Clean Air Act as amended. Public comments were requested on the proposal in the FEDERAL REGISTER publication, and a public hearing was held on November 9, 1979. There were 15 commenters representing coatings manufacturers and suppliers, trade and professional associations, and State air pollution control agencies. The comments that were submitted, along with EPA's responses, are summarized in this document. The summary of comments and responses serves as the basis for most of the revisions that have been made to the test methods between proposal and promulgation. Some of the changes to the proposed test methods are based on additional information obtained by EPA from experience with the methods.

1.1 SUMMARY OF CHANGES SINCE PROPOSAL

A number of changes of varying importance have been made since proposal. One of the most significant of these changes is the Administrator's decision to reject the proposed Method 24 (Candidate 1), Determination of Volatile Content (as Carbon) of Paint, Varnish, Lacquer, or Related Products. Data submitted by coatings manufacturers showed that there are certain coatings which cannot be analyzed using Candidate 1. Therefore, the Administrator has concluded that Candidate 1 is not applicable to all coatings and should not be selected as the reference method.

Several procedural and editorial changes have been made to Reference Methods 24 (Candidate 2), "Determination of Volatile Matter Content, Water Content, Density, Volume Solids, and Weight Solids of Surface Coatings," and Reference Method 25, "Determination of Total Gaseous Nonmethane Organic Emissions as Carbon," in order to clarify and to improve the sampling and analytical procedures. These changes are based on additional information obtained by EPA from experience with the methods and on the public comments received.

Reference Method 24

The following discussion summarizes the procedural changes made to proposed Reference Method 24, Candidate 2. The procedures were added to protect the source owner from invalid results that might result from poor analytical techniques, application of the method to a coating not suitable for analysis with Reference Method 24, or imprecision in Reference Method 24 resulting from a high percentage of water in the solvent.

The promulgated reference method requires the analyst to complete duplicate analyses on each sample tested. A comparison is then made between these results and the within-laboratory precision statements for each parameter. Duplicate analyses are made until the results fall within the range established for the within-laboratory precision statements. The purpose of the procedure is to verify that the analyst can achieve a level of precision for the coating under analysis equal to or better than the precision obtained by experienced analysts participating in the ASTM studies of the method. Because of the variety of coatings that may be subject to analysis, it is possible that certain coatings may not be amenable to analysis using Reference Method 24; that is, in certain cases it may not be possible to achieve results which meet the precision limits. In this case, the method provides for a case-by-case evaluation and development of a suitable procedure.

An additional procedure for waterborne coatings was added to the promulgated reference method to protect the source owner or operator from a determination of noncompliance when the owner is actually in compliance. This procedure is needed because the results of Reference Method 24 are dependent on the difference between the weight of total solvents and the weight of water. As the percent weight of water increases, the difference decreases. As a result, any imprecision in the measurement of the weight of total solvent in water is magnified in the calculation of organic solvent content. For example, if the total solvent of a coating is measured as 100 ± 2 units and the water content is measured at 90 ± 2 units, the organic solvent content would be in the range of 6 to 14 units. The magnitude of the range, as a percent of the true organic solvent content, increases with increasing water content and could, as shown in the example, lead to a conclusion of noncompliance even when the owner is in compliance.

The procedure added to Reference Method 24 for waterborne coatings protects the owner or operator from this erroneous determination by minimizing the calculated value for VOC content. This is done, for example, by subtracting the between-laboratory precision statement from the average value of total solvent and adding the between-laboratory precision statement to the average value for water content. Thus, if a source owner is in compliance based on average coating values, the compliance method will automatically show a lower VOC content because of the adjustments made to the average values based on the between-laboratory precision statements.

Based on comments from manufacturers that ASTM D-2697 has only been shown to be applicable to architectural coatings, the experimental procedure for determining volume solids has been eliminated. Method 24 requires that the volume solids be calculated from manufacturer's formulation data.

The coatings classification step in the proposed method was eliminated because industry comments indicated that it was only necessary to separate waterborne (water reducible) and solvent-borne (solvent reducible) coatings. Therefore, the "Procedure" discussed in Section 4 of the method has been simplified. The elimination of coating classes means that all coatings will be analyzed by the same procedure except for the additional step of measuring the water content of waterborne coatings.

Reference Method 25

The majority of the procedural changes relate to calibration requirements and are meant to improve quality assurance and at the same time simplify the daily operation of the analytical equipment. This is accomplished by requiring a performance test of the analytical equipment

(nonmethane organic analyzer and condensate recovery and conditioning apparatus) prior to initial use; specific criteria for the performance tests are provided. Routine daily calibrations (much less time consuming than previously required) are conducted and the results are compared to performance test reference values to determine whether the performance of the analytical equipment is still acceptable.

Other procedural changes include the following: (1) the addition of pure oxygen carrier gas just prior to the catalyst in the condensate recovery and conditioning system - the auxiliary oxygen is required to assure complete oxidation; (2) the simplification of the pretest and post-test sampling train leak checks; and (3) the calculation changes which are made by including the subtraction of blank values from the measured values.

In the promulgated test method, several important system components are not specified; instead, minimum performance specifications for these components are provided. The method is written in this manner to allow individual preference in choosing components, as well as to encourage development and use of improved components. Therefore, Addendum I which lists specific information regarding system components found to be acceptable has been added to the method to provide guidance for users.

Specifics of the most important procedural changes that have been included in the promulgated test method are as follows:

1. Section 1.1 Applicability. This section was rewritten to clarify the applicability of Method 25 in relation to several other organic measurement methods.

2. Section 2.2.2 Nonmethane Organic Analyzer. The reference to the analyzer is changed from "total gaseous nonmethane organic analyzer" to nonmethane organic analyzer (NMO). The description is clarified to indicate that the NMO analyzer is also used to quantify CO_2 from trap condensate recovery. Furthermore, a requirement that the NMO analyzer meet an initial performance test with specific criteria is added. Previously, only demonstration of "proper separation, oxidation, reduction and measurement" was required.

3. Section 4.1.3 Pretest Leak Check. The leak check procedure is simplified. Instead of evacuating the sample train, the sample probe is plugged and then the sample valve is opened; the sample tank vacuum gauge is monitored for a change in vacuum.

4. Section 4.1.4 Sample Train Operation. This section is clarified to indicate that any probe extension used must be positioned totally in the stack effluent; any portion of the sample probe outside the stack wall must be analyzed as part of the condensate trap.

5. Section 4.1.5 Post Test Leak Check. The leak check procedure is simplified (see "3" above).

6. Section 4.3.3 Recovery of Condensate Trap Sample. A requirement for mixing auxiliary oxygen with the carrier gas just prior to the catalyst is added. The procedures are clarified to indicate that the condensate trap is placed in a muffle furnace at 500°C (changed from 600°C) and that the probe must be heated.

7. Section 5.1 Initial Performance Check for Condensate Recovery and Conditioning Apparatus. A requirement is added for an initial performance test of the system which includes a carrier gas blank value determination (section 5.1.1), an oxidation catalyst

efficiency check (section 5.1.2), and an overall system performance check via liquid injections (section 5.1.3). Previously, only a catalyst efficiency check was required.

8. Section 5.2 Initial NMO Analyzer Performance Test. The calibration criteria for the NMO analyzer are changed to include an initial performance test. This performance test requires an oxidation catalyst check (5.2.1), an analyzer linearity check (5.2.2), determination of a NMO calibration response factor (5.2.2), determination of a CO_2 calibration response factor (5.2.3), determination of a NMO blank value (5.2.4) and a system check using several gaseous organic compounds (5.2.5).

9. Section 5.3 NMO Daily Calibration. This section requires that a daily calibration of the NMO analyzer be conducted. The calibration involves one CO_2 calibration gas and one propane calibration gas. Response factors are determined for both CO_2 and NMO, and a NMO blank value is measured. This calibration is conducted with the oxidation and reduction catalysts in full operation. The results obtained are compared to the reference values obtained during the initial performance test in order to determine if the analyzer performance is acceptable. This daily calibration procedure is greatly simplified compared to the procedure previously required which included bypassing the oxidation and reduction catalysts and using several different concentration levels of methane, carbon dioxide and propane calibration gases.

10. Section 6.2 Noncondensible Organics. The calculation for the NMO concentration of the contents of each collection tank is changed by

rewriting the equation to include the subtraction of the daily NMO blank value from the measured concentration.

11. Section 6.3 Condensible Organics. The calculation for the NMO concentration of the contents of each condensate trap is changed by rewriting the equation to include the subtraction of the daily condensate recovery and conditioning system carrier blank value from the measured CO_2 concentration.

CHAPTER 2

SUMMARY OF PUBLIC COMMENTS

The list of commenters and their affiliations is shown in Table 2-1 of this chapter. Fifteen letters contained comments on the proposed test methods. The comments and issues and responses to them are discussed in the following section of this chapter.

2.1 TEST METHODS

2.1.1 Comment: Most commenters objected to using the carbon approach to measuring emissions and to the use of Method 24 (Candidate 1).

Response: Based on data submitted by coatings manufacturers, there are some coatings that cannot be analyzed using Method 24 (Candidate 1). These coatings cannot be distilled because they foam vigorously upon heating, thus contaminating the distillate. In addition, the data indicated that less than 90 percent of the solvent would be recovered during the distillation step for certain coatings. Since the distillation step is essential for determining the carbon content and density of the solvent, EPA is withdrawing this procedure from further consideration at this time.

2.1.2 Comment: Several commenters objected to the use of ASTM D-2697 to determine the density of the dried coating as required in Method 24 (Candidate 2). A number of commenters noted that ASTM D-2697 was not specifically applicable to certain coatings. It was also

suggested by one commenter that EPA should specify volume fraction of solids for the various types of coatings similar to the way transfer efficiencies were listed.

Response: Based on comments from manufacturers that ASTM 2697 has only been shown to be applicable to architectural coatings, the experimental determination of volume fraction of solids has been eliminated. Method 24 will require that the volume fraction of solids be calculated from manufacturer's formulation data.

2.1.3 Comment: Another commenter noted that the drying time was different for ASTM D-2369 and ASTM D-2697 and that these procedures were not consistent with each other.

Response: Since ASTM D-2697 has been deleted, this comment is no longer applicable.

2.1.4 Comment: One commenter requested that analyzing a single composite sample (of all coatings used in an operation) be allowed rather than analyzing each coating and taking an arithmetic average. Would there be any complications caused by mixing several coatings and then running a Method 24 (2) analysis on the mixture?

Response: EPA has no information on the consequences of mixing coatings before analysis. This would be acceptable on a case-by-base basis as allowed in 40 CFR 60.8(b) if the owner or operator could demonstrate to the Administrator's satisfaction that the mixing of coatings before analysis would not produce different results than analyzing the samples separately.

2.1.5 Comment: Several commenters recommended that the use of coatings manufacturers' data be allowed in calculating VOC content of coatings rather than Method 24.

Response: Coatings manufacturers' data will be allowed in calculating VOC content of coatings because this will reduce the burden on the industry to measure all coatings with Method 24. Method 24 will be the reference method. Use of this method to calculate VOC content of coatings will require industries to closely monitor and record all organic solvents added to the coatings at the plant.

2.1.6 Comment: Three commenters recommended that the direct use of a flame ionization detection (FID) system or similar instrumentation system be allowed instead of Method 25 because: (a) direct FID is simpler and more precise and (b) the ability to conduct on-site analyses and DOT restrictions associated with shipping organic samples from a source location to a laboratory make the FID preferable.

Response: While the direct use of an FID system is simpler than Method 25, it will not give accurate results in many situations because the instrument response varies with different compounds. Data collected to date indicate that the FID will give calculated incineration efficiencies which may be biased high (relative to Method 25) as much as 5 percent (i.e., 99 percent efficiency with FID vs 94 percent efficiency with Method 25). Therefore, the FID system cannot be considered an adequate reference method, but may be acceptable as an alternative compliance procedure on a case-by-case basis as allowed in 40 CFR 60.8(b).

The ability to use the FID system to conduct on-site analyses is not itself sufficient justification to allow the use of direct flame ionization detection. The DOT regulations for the shipping of hazardous materials do require that great care be taken in shipping the test samples. The DOT regulations impose strict packaging

requirements on flammable liquids and compressed flammable gases. Flammable liquids must be marked as such and must be shipped as hazardous materials. However, exemptions for the strict packaging requirements are permitted for most liquids (49 CFR 172.101) if less than 1 quart is shipped. The volume of a sample trap is 0.1 pint. Assuming all traps were completely full of organic liquid, as many as 20 traps could be shipped in one container. In addition, gas sample tanks likely to be shipped from an on-site location to a laboratory do not meet the DOT definition of a compressed flammable gas (49 CFR 173.300) because they are not under high pressure and, therefore, should not pose a shipping problem. For "unknown" environmental samples, the DOT regulations (49 CFR 172.402) require labeling according to the most likely class assignment (e.g., flammable liquid) and any additional knowledge about the sample that the shipper may have. Therefore, while the DOT regulations do require careful attention when shipping test samples, the regulations will not restrict the shipment of test samples from an on-site location to a laboratory.

2.1.7 Specific comments on the procedures of Method 25 are underlined below. EPA's responses follow.

(a) The sample probe should contain a heated filter. Presently, there is no data available to support the requirement for a filter in the sampling train. However, it is recognized that organic particulate matter will interfere with the analysis and, therefore, in some cases an in-stack particulate filter will be required (as noted in Section 1.1 of the method). EPA will continue to investigate this matter and, if appropriate, a change will be made.

(b) Problems have been encountered with locating suitable collection vessels. The method specifies aluminum or stainless steel tanks. Several vendors of suitable tanks have been located. Therefore, aluminum or stainless steel vessels will continue to be required.

(c) An accurate vacuum gauge should be substituted for the mercury manometer for in-field use. The data presented with the comment was not sufficient to justify a change in the proposed method; therefore, no change was made. However, a vacuum gauge would be considered an acceptable alternative as allowed in 40 CFR 60.8(b) if the user could demonstrate to the Administrator's satisfaction that it was as accurate as the mercury manometer.

(d) Specific details of the total gaseous nonmethane organic analyzer should be given in the reference method. Specific details of the analyzer were intentionally deleted to permit various designs to be used. Only the performance of the analyzer is critical, and performance criteria are given in the method. Addendum I, which lists specific system components, has been added to the promulgated method to provide guidance for users.

(e) Specific catalysts should be cited in the method. Only performance specifications for the catalysts are given in order to permit use of different catalysts. Some catalysts that have been found to be acceptable are cited in the addendum to the promulgated Method 25.

(f) Initial tank evacuation and pressure measurement should be made only in the laboratory. If good technique is followed, this can be conducted in the field. Therefore, the recommendation will not be included in Method 25.

(g) The post-test leak check is overcomplicated, and the same result could be obtained by simply plugging the probe and monitoring for a pressure drop. This approach does simplify the procedure, and the method has been modified.

(h) The final tank pressure/temperature should be measured following a 24-hour equilibration period. Such a long equilibration period should not be necessary. Except for extreme conditions (i.e., winter sampling), a period of less than 1 hour should be sufficient. Given the "worst case" conditions, in which the pressure was immediately measured after sampling at 35°C or -7°C and the incorrect gas temperature of 20°C was assumed, the errors in the calculated sample volume would still be only +5.2 percent and -2.5 percent, respectively.

(i) An equilibration period should be required before measuring the final tank pressure. The tank contains enough surface area and mass to assure that the internal gas temperature will be at ambient conditions. Therefore, no equilibration period will be required.

(j) Directions should be provided for heating the sampling probe because this tubing can contain organics. Directions for heating the probe have been added to the method.

TABLE 2-1

LIST OF COMMENTERS ON PROPOSED TEST METHODS 24 AND 25
Docket No. A-79-05

Document No.	Commenter/Affiliation
D-1	William T. Cavanaugh, Managing Director ASTM 1916 Race Street Philadelphia, Pennsylvania 19103
D-1a	H. J. Stremba, Deputy Managing Director ASTM 1916 Race Street Philadelphia, Pennsylvania 19103
D-2 and D-2a	John E. Lowe Environmental Coordinator Finishes Division E.I. DuPont De Nemours & Company Wilmington, Delaware 19898
D-3	Larry L. Thomas, Executive Director National Paint and Coatings Association 1500 Rhode Island Avenue, N.W. Washington, D. C. 20005
D-4	Robert H. Collom, Chief Air Protection Branch State of Georgia Department of Natural Resources Environmental Protection Division 270 Washington Street, S.W. Atlanta, Georgia 30334
D-5	Victoria Hathaway-Sarver Air Pollution Control Specialist Abatement Unit Regional Air Pollution Control Agency 451 W. Third Street P.O. Box 972 Dayton, Ohio 45422
D-6	R. J. Anderson, Vice President DeSoto, Inc. 1700 South Mount Prospect Road Des Plaines, Illinois 60018
D-7	W. R. Johnson, Director Plant Environment Environmental Activities Staff General Motors Corporation Warren, Michigan 48089

Document No.	Commenter/Affiliation
D-8	C. B. Potelunas, Manager Air and Water Pollution Control American Motors Corporation 14250 Plymouth Road Detroit, Michigan 48232
D-9	R. W. Vorhees, Manager Environmental Engineering & Manufacturing Standards Crysler Corporation P.O. Box 1919 Detroit, Michigan 48288
D-11	A. B. M. Houston, Manager Compliance and Liaison Department Stationary Source Environmental Control Ford Motor Company One Parklane Boulevard Dearborn, Michigan 48126
D-12	Delbert Rector, Chief Air Quality Division State of Michigan Department of Natural Resources Stevens T. Mason Building Box 30028 Lansing, Michigan 48909
D-14	Daniel J. Goodwin Manager, Division of Air Pollution Control Illinois EPA 2200 Churchill Road Springfield, Illinois 62706
D-15	J. C. Weaver, Chairman of D01-21-13 Task Group on VOC ASTM 1916 Race Street Philadelphia, Pennsylvania 19103